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**New Developments in Second-Order Nonlinear Optical Polymeric  
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**by**

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## NEW DEVELOPMENTS IN SECOND-ORDER NONLINEAR OPTICAL POLYMERIC MATERIALS

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### ABSTRACT

Second harmonic generation from the spin coated films of an asymmetrically substituted polydiacetylene, namely poly((8-butoxy carbonyl)methyl urethanyl) 1-(5-pyrimidyl)-octa-1,3-diyne(BPOD) is reported for the first time. The macromolecules assemble to produce the organization responsible for SHG without recourse to poling.  $d_{33}$  of the spin coated film (0.19-0.31  $\mu\text{m}$  thickness) are between 0.78-0.88 pm/V without absorption correction and 3.32-5.57 pm/V after correction. Angular and polarization dependence study of the second harmonic response suggests that the film has in-plane isotropy as a whole and the net dipole is nearly perpendicular to the film surface. Spontaneous orientation of the polymer chains during the film formation seems to be responsible for the noncentrosymmetric alignment of the polymer. SHG from the Langmuir Blodgett films are also reported.

### INTRODUCTION

There has been a great interest in polymeric materials as potential candidates for nonlinear optical applications. Polydiacetylenes(PDAs) are a class of conjugated polymers and one of the promising candidates for these applications owing to their large third order susceptibilities [1] and ultrafast response( $\chi^{(3)} \sim 10^{-9}$ - $10^{-10}$  esu) [2,3]. PDAs can be obtained in various forms and the third harmonic generation in solutions [4], in single crystals [1], and in thin films [5,6] has been reported previously. It has been suggested that PDAs with aromatic substituents directly attached to the main backbone will present novel properties for these applications since the number of  $\pi$ -electrons per repeating units increases through  $\pi$ -conjugation between the backbone and the sidegroups [6,7-8].

Second harmonic generation is not expected in PDAs due to their centrosymmetric nature. However electric-field-induced second harmonic generation(SHG) in PDA films [9] has been reported in which the

symmetry is broken due to the external DC-field. Berkovic et al. [10] observed SHG in the monolayers of several diacetylenes monomers and polymers spread at the air-water interfaces in a Langmuir Blodgett(LB) trough. They believed that the SHG signals arise mainly from the sidegroups on the PDAs since the diacetylene core is centrosymmetric. Garito et al. [11] demonstrated the significant electric-field-induced SHG from PDAs containing two different, highly asymmetric substituents (one is NLO active chromophore). They concluded that the magnitude of the macroscopic NLO response in PDAs critically depend on the nature of the microscopic charge correlated  $\pi$ -electron states and also on the symmetry and the degree of the structural order.

Recently we have reported a soluble, asymmetrically substituted PDA, viz. poly((8-butoxy carbonyl)methyl urethanyl) 1-(5-pyrimidyl)-octa-1,3-diyne(BPOD), in which an aromatic substituent is directly attached to the main backbone [12].

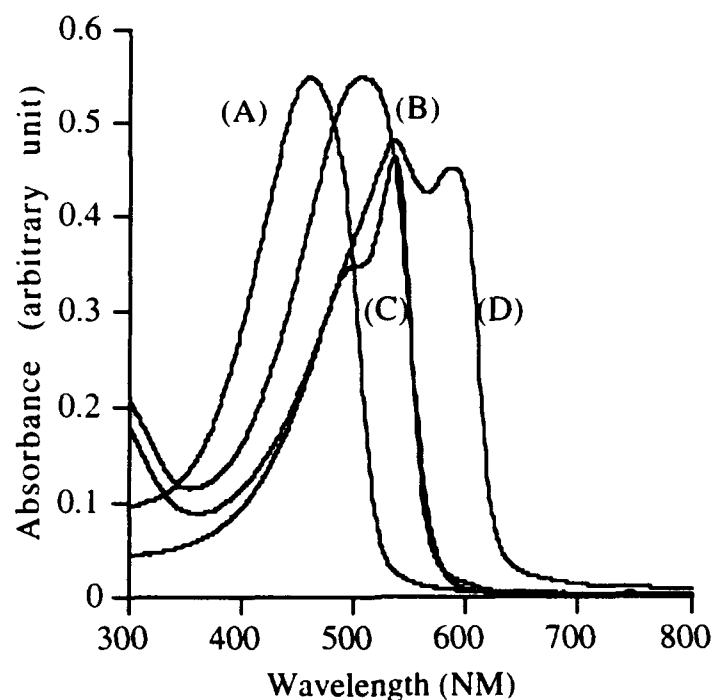


Figure 1. Absorption spectra of poly(4-BCMU) and poly(BPOD). (A) and (B): in chloroform (C) and (D): in chloroform/hexane, respectively.

Poly(BPOD) is highly soluble in chloroform and this good solution shows a  $\lambda_{\max}$  at 510nm(red)(figure 1-B). Upon the addition of nonsolvents such as hexane and ethanol, poly(BPOD) shows a dramatic color transition from red to purple(599nm)(figure 1-D). Absorption spectra of poly(BPOD) in good and poor solutions are shown in figure 1 and are compared with those of poly(4-BCMU). The only structural difference in poly(BPOD) from that of poly(4-BCMU) is that the former has one of the flexible urethane sidegroups replaced by a rigid aromatic pyrimidyl group. The differences in the  $\lambda_{\max}$  between poly(4-BCMU) and poly(BPOD) in the poor solutions as well as good solutions clearly indicate that the effective conjugation in poly(BPOD) is enhanced through conjugation between the main backbone and the aromatic sidegroups. Poly(BPOD), with its enhanced conjugation length, is an ideal candidate for the investigation of NLO properties since various forms of the polymer can be obtained such as single crystal, solution, and optical quality spin on films.

In this paper, we present for the first time the second harmonic generation (SHG) in an amorphous spin coated films of poly(BPOD). External electric fields were not employed to produce the poled alignment. We speculate that the SHG signals are mainly due to the spontaneous orientation of the sidegroups during the film formation process. This type of process dependent orientation has been observed in spin coated films of polyimides [13,14]. SHG from the LB monolayer and multilayers of poly(BPOD) are also reported.

## **EXPERIMENTAL**

### **Thick film formation**

Synthesis and solid state polymerization of diacetylene monomer BPOD has been reported elsewhere [12]. Single crystals of poly(BPOD) were dissolved in chloroform(~1% w/v) and the films were obtained either by spin coating or casting the polymer solutions on glass substrates. Solvent was slowly evaporated in the case of cast film and both types of films were dried overnight under vacuum. The film thickness was in the range of 0.2-0.5 $\mu$ m for spin coated sample and 2-4 $\mu$ m for cast film.

## LB monolayer formation

All monolayer studies were carried out on a Lauda MGW Filmwaage trough. The surface pressure-area isotherm of poly(BPOD) was obtained by spreading the chloroform solution (0.5 mM) onto a purified Milli-Q water surface at 20°C and compressing the polymer at a speed of 2 mm<sup>2</sup>/min until collapse of the film was observed. Monolayers were transferred to a glass substrate at various surface pressures.

## Instrumentation and SHG measurement

Absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. SHG measurements were carried out according to the method reported earlier [15].

## RESULTS AND DISCUSSION

### SHG in spin coated film

An estimate of the effective d-coefficient for the spin coated films has been obtained by assuming the tensor properties of the films to be of similar nature as the poled polymeric systems [16]. The  $d_{\text{eff}}$  for the spin coated films of poly(BPOD) are summarized in Table 1.

Table 1.  $d_{33}$  values for poly(BPOD) spin coated samples at incident wavelength of 1.06  $\mu\text{m}$ .

Film thickness ( $\mu\text{m}$ )	$d_{33}$ (pm/V)	
	w/o abs. correction	with abs. correction
0.31	0.74	5.57
0.25	0.78	4.43
0.19	0.88	3.32

Transmission Electron Microscopy (TEM) and X-ray diffraction as well as Polarized Optical Microscopy study indicate that the films are amorphous and no crystallinity is present. However, a couple of small humps at low angles of X-ray diffraction pattern suggest the presence of certain degree of orientation in the film. Two broad rings from the diffraction pattern from TEM also support the results of the X-ray study.

It is speculated that the SHG signal of the films arises from the spontaneous alignment of the molecules because of the interaction between negatively charged glass substrate and positively charged pyrimidyl rings.

The angular and polarization dependence of the second harmonic signal from the poly(BPOD) thin films show a behavior similar to the poled second order nonlinear polymers. Figure 2 shows the SH intensity as a function of the polarization angle( $\phi$ ) of the incident fundamental beam for a spin coated film. The second harmonic polarization was selected as p-polarization. The angle of incidence for fundamental beam was kept at  $45^\circ$ . The values shown in figure 2 gives a nearly perfect fit to a function of  $(A\sin^2\phi + B\cos^2\phi)^2$  which indicates that these films have in-plane isotropy.

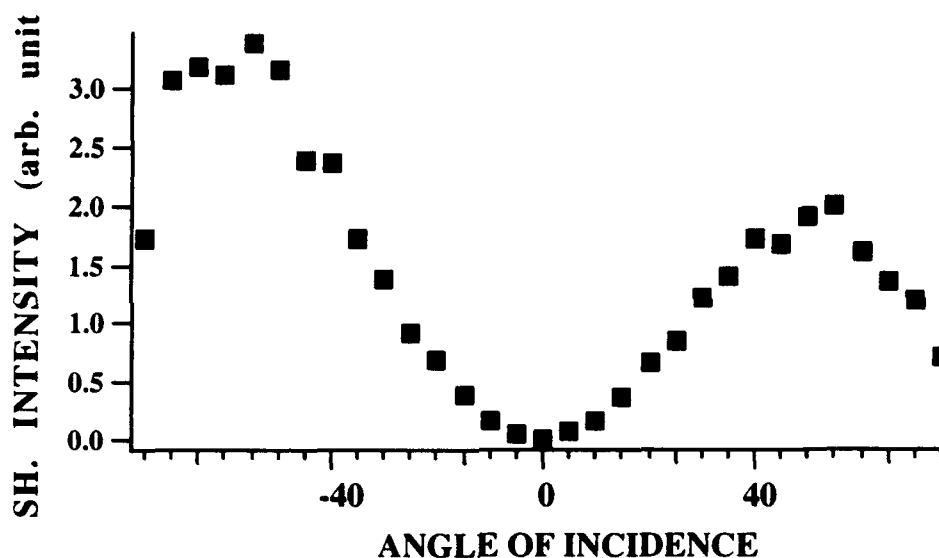


Figure 2. Plot of angle of incidence vs SH intensity of spin coated film of poly(BPOD).

Angular dependence of the second harmonic signal from spin coated poly(BPOD) is shown in Figure 3. SH intensity reaches a maximum when the incident fundamental beam is at  $40^\circ$  with respect to the substrate plane and becomes zero at normal incidence. No second harmonic response is expected for the fundamental beam incident normal to the substrate if the c-axis (optic axis) in the film is aligned perpendicular to the substrate plane. This suggests that the net dipole moment of the polymer film is nearly perpendicular to the substrate plane.



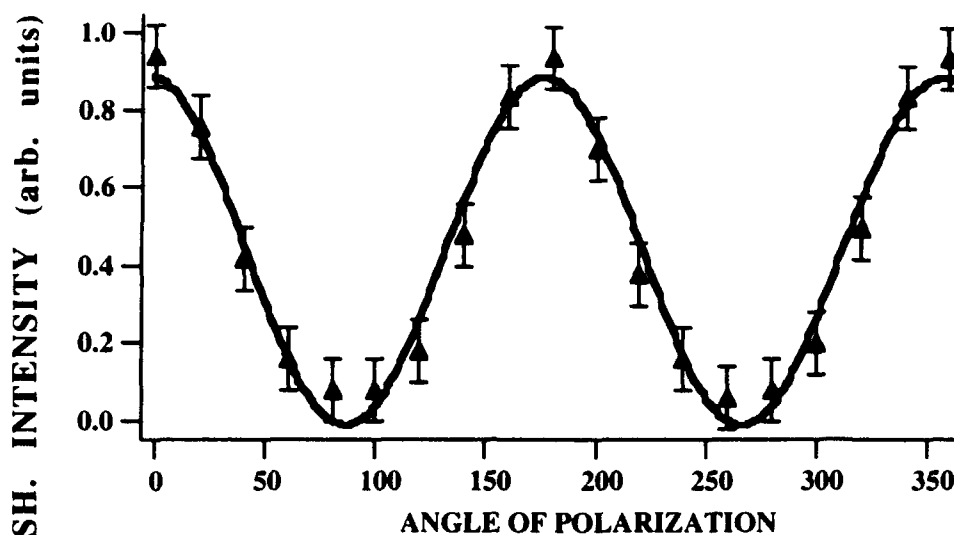


Figure 3. Plot of polarization angle vs SH intensity of spin coated film of poly(BPOD).

### SHG in LB film

Absorption spectra of poly(BPOD) LB films consisting of a single layer and four layers are shown in figure 4. A higher absorption from four layered LB film indicates the formation of multilayer. The s- and p-polarized absorption spectra of the monolayer are also shown in figure 5. The difference in the absorption intensity between the two polarized light suggest the presence of anisotropy in the film.

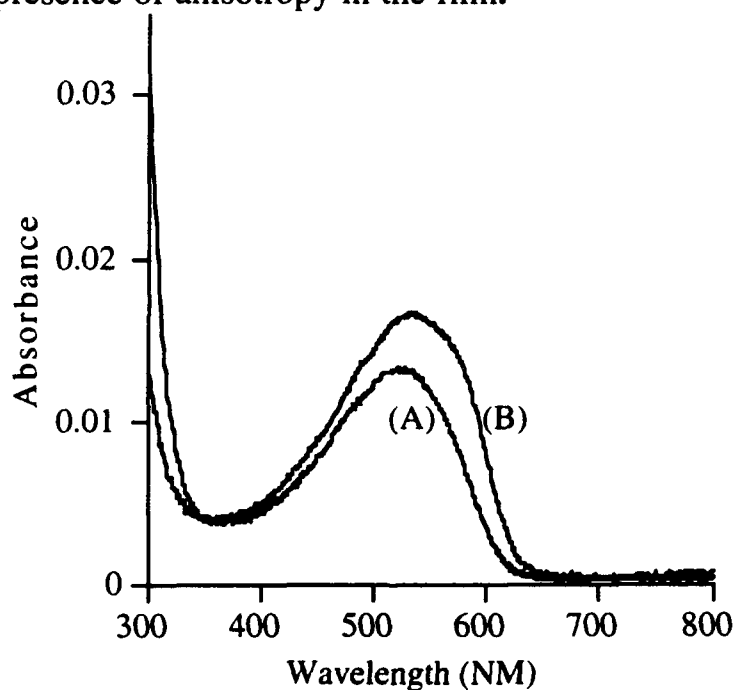


Figure 4. Absorption spectra of poly(BPOD).  
(A) one layer (B) four layers.

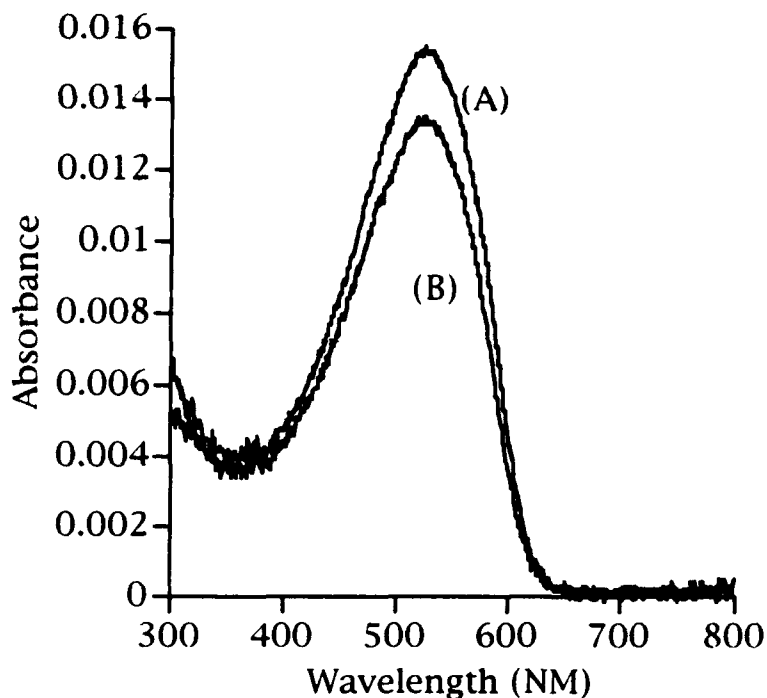


Figure 5. Absorption spectra of poly(BPOD) monolayer. (A) s-polarized light (B) p-polarized light. Incident beam is in the perpendicular direction to the film surface.

Typical surface-pressure area isotherm is shown in figure 6 and SH intensities from monolayers obtained at different surface pressure are summarized in Table 2. The SH intensity reached maximum at the surface pressure of 15mN/m. Fine fibers started to form during the monolayer formation when the surface pressure is higher than 20 mN/m. It appears that the noncentrosymmetric nature of the film is broken at higher surface pressure and results in a fiber formation as the chains collapse together. These fibers were found to be crystalline under polarized optical microscopy. For comparison, monolayers of poly(4-BCMU) were obtained by similar method. Fiber formation was not observed even at higher surface pressure and no measurable SH signal was shown from the monolayers of poly(4-BCMU). Comparison of the chemical structure of poly(BPOD) and poly(4-BCMU) suggests that the SH signals observed in poly(BPOD) must arise from the asymmetric nature of the sidegroups and their interaction with the conjugated backbone. Noncentrosymmetric character in the film is introduced possibly due to the interaction between the negatively charged glass substrate and partial positive charge on the pyrimidyl ring.

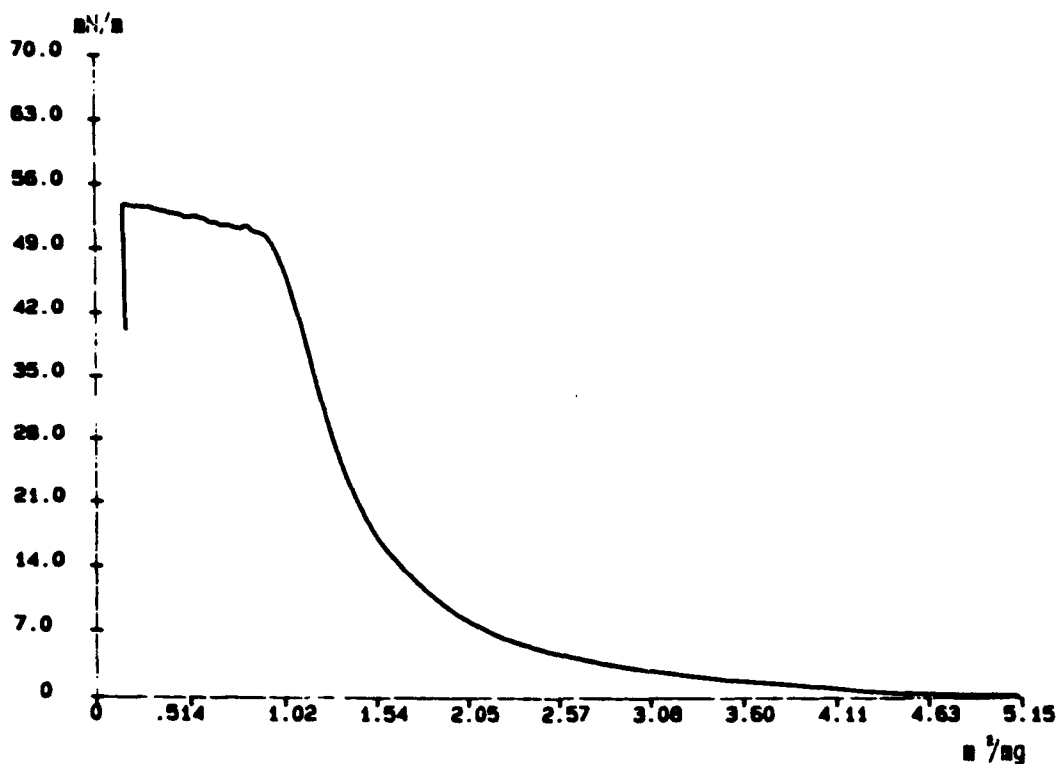


Figure 6. Surface-pressure area isotherm of poly(BPOD).

Table 2. Second harmonic signals from poly(BPOD) monolayer at different surface pressure.

Surface pressure (mN/m)	SH signal
10	-0.60
15	-1.39
20	-1.12
25	-0.65

\* Y-cut crystal quartz (3.0 mm thick) was used as a reference and the SH intensity from quartz was approximately 5 orders of magnitude higher than the monolayers.

## CONCLUSION

Second harmonic generation from the spin coated films and Langmuir Blodgett films of asymmetric polydiacetylene, namely poly((8-butoxy carbonyl)methyl urethanyl) 1-(5-pyrimidyl)-octa-1,3-diyne(BPOD) is reported for the first time.  $d_{33}$  of the spin coated films (0.19-0.31  $\mu\text{m}$  thickness) are between 3.32-5.57 pm/V after absorption correction. SHG signals from the films seem to arise from the spontaneous alignment of the polymer chain during the film formation which result in a noncentrosymmetric rearrangement of the chains.

## ACKNOWLEDGMENTS

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